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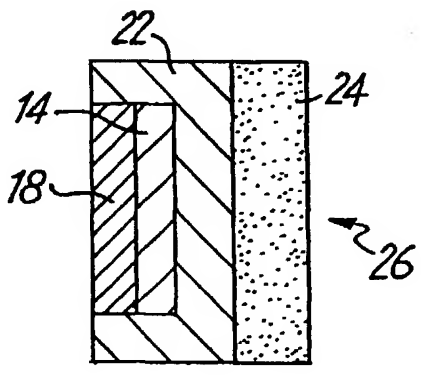
(54) Title: IN-MOLD DECORATIVE TRANSFER AND PROCESS



(57) Abstract: Improved inks are used to create decorative transfers. The inks include a polymer base that is crosslinkable when exposed to a catalyst. Methods for making molded products with an image that is visible through and protected by a crosslinked clear outer gel coat (18) are described. Preferred methods include the use of decorative transfers that have an image layer (14) created with ink containing a crosslinkable polymer base.

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IN-MOLD DECORATIVE TRANSFER AND PROCESS

BACKGROUND OF THE INVENTION

The present invention relates to decorative transfers. In particular, the invention relates to decorative transfers with a backing sheet and an image layer formed with improved inks. The present invention also relates to applying decorative transfers during a molding process to produce an image embedded within the molded product.

Decorative transfers are applied to a number of functional objects, for example, boats, cars, planes, showers, and to a variety of decorative objects. Decorative transfers may contain images that are decorative and/or informative.

The application of decorative transfers to a number of different products can be based on a pressure sensitive adhesive for applying the transfer to the exterior of the molded product. The process includes die cutting, kiss cutting and premasking to prepare the graphic for application. Potential problems with delamination of the transfer exist, as well as with chemical reactions between incompatible materials. Similarly, water slide transfer decals that are essentially paper backed decals which provide for separation of the decal from the backing paper upon the application of water to the backing paper have been used to generate a transfer with a tacky adhesive upon the application of water.

SUMMARY OF THE INVENTION

In a first aspect, the invention pertains to a decorative transfer including a backing sheet and an image layer on the inner surface of the backing sheet. The image layer includes a film of an ink having a crosslinkable polymer base.

In a further aspect, the invention pertains to a molded product including an image layer and a clear outer gel coat covering the image layer. The clear outer gel coat includes a polymer that is crosslinked.

In another aspect, the invention pertains to a process of providing a decorative transfer including the step of creating an image onto a backing sheet. The image is screen applied to the backing sheet with an ink that crosslinks upon exposure to a catalyst.

In a further aspect, the invention pertains to a process for making a molded product with a decorative transfer. The method includes applying a clear outer gel coat onto a mold surface wherein the clear outer gel coat attains a tacky surface. A decorative transfer that includes an image layer and a backing sheet is placed onto the tacky surface of the clear outer gel coat with the image layer in contact with the tacky surface.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a cross-sectional view of a decorative transfer with an image applied to the inner surface of a backing.

Fig. 2 is a cross-sectional view of a typical mold that has a clear outer gel coat on the mold in a tacky state and a decorative transfer as shown in Fig. 1.

Fig. 3 is a cross-sectional view of a mold with the image laminated to the catalyzed but not fully cured clear outer gel coat and a color gel coat.

Fig. 4 is a cross-sectional view showing a molded product removed from the mold surface. The image layer is sandwiched and permanently bonded in place between the clear outer gel coat and the color gel coat.

DETAILED DESCRIPTION OF THE ILLUSTRATIVE EMBODIMENTS

Improved decorative transfers, commonly called "decals", generally are produced with a backing and an image layer that is in contact with the inner surface of the backing. Desired images are created on the decorative transfers using improved inks. The inks preferably include polymers that can be crosslinked upon exposure to a catalyst. In preferred embodiments, the polymer base of the inks, used for creating the image layer, is chemically compatible with the polymer base of a clear outer gel coat of a desired molded product to which the image is ultimately bonded.

The molded products of this invention include a clear outer gel coat and an image protected by the crosslinked clear outer gel coat. Preferably, in the molded products, the polymer base of the inks used to create the image are also crosslinked. The

molded products also include a color gel coat and a molded structure that comprises substrates and crosslinked resin. The polymers in all of the layers preferably have been co-crosslinked in the molded products described herein.

The images on the decorative transfers can be incorporated into molded products by improved methods. A clear outer layer resin, referred to herein as the clear outer gel coat, can be applied to a mold surface, preferably to a defined area. The clear outer gel coat can acquire a tacky or sticky gel state and upon exposure to a catalyst, it can crosslink. The decorative transfer can be placed on the tacky clear outer gel coat with the image layer in contact with the tacky surface of the clear outer gel coat. The inks preferably have a crosslinkable polymer base. The polymer base of the inks and the polymer base of the clear outer gel coats are preferably chemically compatible, more preferably equivalent. The backing of the decorative transfer can be removed after the image has been adhered to the tacky clear outer gel coat.

After removing the backing layer, a color gel coat can be applied onto the mold surface and over the clear outer gel coat and the image layer. The color gel coat preferably is applied prior to complete crosslinking of the polymer bases on the mold surface, i.e. the clear outer gel coat and the ink, if using ink with crosslinkable polymer base. A molded structure can be formed further by applying, over the color gel

coat, one or more substrates such as fiberglass mats along with a crosslinkable support resin. Preferably, a plurality of substrates are layered with a crosslinkable support resin between each layer. Crosslinking of the various polymers on the mold surface concurrently will be referred to herein as co-crosslinking. Co-crosslinking of the clear outer gel coat, the ink polymer base, the color gel coat and the support resin of the molded structure can result in molded products with a monolithic structure with the image embedded between crosslinked polymers.

In Figure 1, a decorative transfer indicated generally at 10 includes a backing 12 on which an image represented as a layer 14 is applied on the inner surface of the backing 12. In preferred embodiments, the backing 12 is a water slide liner. The image is, preferably, created with ink that includes polymers that are compatible with polymers in the clear outer gel coat to which the image is ultimately bonded. By "compatible", it is meant that the polymers in the specified layers, upon crosslinking, form a band that is seamless to visual observation.

The backing is used to provide a surface to create the image and to transport the image or decorative design to its desired location. Images can be created on the backing with inks using a variety of techniques. The inks used to create the image on the backing can form a dry surface after a period of time. Thus, the image may be dry to the touch prior to

contact with the clear outer gel coat. Preferably, the images are created by screenprinting. The images of the decorative transfers are applied to the inner surface of the backing and can be firmly attached to the backing until a release agent is applied.

The images generally will not release, even during application of the image against the desired surface, for example, the catalyzed but non-cured clear outer gel coat. The images will generally release when the appropriate release agent is applied to the backing. In embodiments using water slide liners as backing, the image generally will not release until water is applied to the backing. Water dissolves a water soluble coating on the backing allowing the image layer to transfer off the backing. Since the image is applied to the mold prior to the formation of the product, no adhesive is required between the backing sheet and the image.

Decorative transfers described herein, preferably, have images that are created using ink polymers that are selected to be compatible with a clear outer gel coat in a process for protecting the image. The images on the decorative transfers can become part of the molded product. The images are not prone to delamination and are protected over prolonged use of the molded product.

The images on decorative transfers can be incorporated into molded products, i.e. boats, snowmobiles, jet skis and bathtubs, using the processes

described herein. Suitable molded products can be any products that are made by the use of a mold surface as a tool to apply a number of polymers and substrates.

An outer gel coat, preferably a clear outer gel coat and more preferably a polyester gel coat, is applied to a mold surface. A clear outer gel coat as referred to herein is generally transparent and includes any gel coat through which an image can be viewed. The clear outer gel coat may include a catalyst for curing or crosslinking. Alternatively, a catalyst in the clear outer gel coat may not be added if the subsequent layers have resins that contain an appropriate catalyst. The catalyst in subsequently applied polymers can catalyze the crosslinking of the clear outer gel coat. The clear outer gel coat generally becomes tacky and sticky after being applied to the mold surface.

If a catalyst has been incorporated into the clear outer gel coat, the clear outer gel coat can be in the tacky state for sometime, prior to becoming completely crosslinked or cured. Alternatively, if a catalyst has not been incorporated into the clear outer gel coat, the clear outer gel coat can retain the tacky state until exposure to a catalyst. Upon exposure to a catalyst, the clear outer gel coat can become completely crosslinked over a period of time. The crosslinked clear outer gel coat can be a hard, resilient structure.

The decorative transfer is generally applied to the clear outer gel coat during the tacky state. The decorative transfer is placed such that the image layer of the decorative transfer contacts the tacky surface of the clear outer gel coat. The image will be visible in the final product through the cured, clear outer gel coat.

In Figure 2, a mold is illustrated in cross section at 16. The mold can be made of any desired materials, for example, metals such as steel and aluminum, fiberglass, polyester, epoxy, silicone and the like. The mold 16 is shaped to the desired configuration for the finished product, such as a boat hull. A clear outer gel coat layer 18 is applied to the mold surface in a conventional manner. There generally is a conventional mold release coating on the mold surface. The polymers in the clear outer gel coat are preferably compatible with, more preferably equivalent to, the polymer base in the ink of the image. Equivalent as referred to herein relates to the presence of the same polymer base in the indicated components.

Referring to Fig. 2, the decorative transfer that includes the image layer 14 and its backing 12 can be applied against the clear outer gel coat layer 18 with the ink side against the tacky surface of the clear outer gel coat layer. The backing from the decorative transfer can be removed after the image is sufficiently adhered to the tacky surface of the clear

outer gel coat. In preferred embodiments, the backing 12 can be removed by applying a release agent such as water. The removal of the backing is represented schematically in Fig. 2 in dashed lines as being lifted off image layer 14. Since the backing is removed with the image held by the tacky outer gel coat, the image transferred, preferably, is not stretched, wrinkled, or buckled or in any way misaligned or damaged.

As shown in Figure 3, in preferred embodiments, after the image 14 is in place, and the backing 12 has been removed, a catalyzed color gel coat 22 can be applied. The color gel coat may be applied over the image layer and the clear outer gel coat. Catalyzed gel coats as referred to herein are gel coats with catalyst that have not yet become fully crosslinked. The color gel coat is also generally applied to the areas of the mold surface that do not contain the clear outer gel coat and the image. The color gel coat generally has a polymer base that is compatible, preferably equivalent, with the polymer base of the clear outer gel coat. A molded structure is generally formed over the color gel coat. The molded structure includes one or more layers of substrates such as fiberglass and carbon fibers, interspersed with crosslinkable support resin.

Once the polymers in the clear outer gel coat, the image, the color gel coat, and the support resin are crosslinked, the molded product may be removed from the mold. As shown in Fig. 4, in the

molded product 26, the ink layer 14, originally on the decorative transfer, is embedded between the clear outer gel coat 18 and the color gel coat 22. The molded structure 24 is overlayed on the color gel coat 22. The image, when made with crosslinkable ink, is generally crosslinked due to the catalyst present in the clear outer gel coat and/or the color gel coat.

In preferred embodiments, the polymer base of the ink used for printing the image on the decorative transfer is an unsaturated polyester resin that can be crosslinked upon exposure to a catalyst. Thus, over time all the polymers in the molded product are exposed to a catalyst from the clear outer gel coat, the color gel coat and/or the support resin. The polymers can be co-crosslinked, i.e. co-cured, to form a particularly desirable, durable product with a monolithic-type structure. A particular advantage is that the image, even after prolonged use, will not separate from the molded product since it is embedded within the product.

The molded product 26, as shown in Figure 4, generally is rigid and after removal from the mold 16 is ready for use and/or additional assembly of fabrication operations. The image in the molded product is visible through and protected by the clear outer gel coat that has a hard abrasion-resistant surface.

A. Decorative Transfer

Referring to Fig. 1, the decorative transfer 10 described herein includes a backing 12 and an image layer 14. The backing includes an inner surface that is in contact with the image layer. A variety of backings are known in the art and are suitable for use for the decorative transfers described herein. Generally, desirable backings can be selected such that separation of the backing from the image does not result in perceivable distortion of the image. Suitable backings can include water release backings, such as a water slide liner, silicone treated paper, silicone treated plastic and the like.

Water release transfer papers, called water slide papers, are disclosed in U.S. Patent 4,337,289 to Reed entitled "Water release transfer", and various processes have been advanced for applying decorative coatings, but none using the materials and processes of the present invention. A process that affixes a decorative pattern to a sticky molded component is shown in U.S. Patent No. 4,490,410 to Takiyama et al. entitled "Method of affixing a decorative pattern to a stock or a molded component". It involves a different process from the present process, and the backing is not separated from the image until the resin coated body is cured.

Generally speaking, it is convenient to apply the image to a water release backing that generally includes a water permeable paper coated with

a water soluble polymer, natural or synthetic, such as dextrin. In these embodiments, when water is applied to the backing, the water permeates the water permeable paper and dissolves the dextrin. The image, thus, is released from the backing paper when the dextrin is solubilized. It will be appreciated that other types of flexible substrates and water-release coatings of other kinds may be used as alternatives. In preferred embodiments, the backing is a water release backing paper.

The image layer on the inner surface of the backing in the decorative transfer can be created using a variety of inks. Suitable inks preferably include polymers that can be crosslinked upon exposure to a catalyst. Furthermore, suitable inks can be selected to have polymer bases that are compatible with the polymer base of a clear outer gel coat to which the image is ultimately bonded.

The image layer may also be created using inks that are not crosslinkable. These inks include vinyl process inks, acrylic process inks, lacquers and the like. It will be understood that the image layer of the decorative transfer can be created using any of the inks generally known for silk screening methods.

The inks can include a polymer base, pigments, and solvents. The inks may, optionally, include gelling agents to control viscosity, flow agents, ultra violet light abosorbers and other suitable compounds.

The polymer base of the inks can include polyester resins, preferably unsaturated polyester resins. Polyester resins can include ortho resins, iso resins, bisphenol A fumarates, chlorendics and vinyl esters. Polyesters generally are formed by the reaction between polyfuctional acids/anhydrides and polyhydroxyl alcohols and preferably between difunctional carboxylic acids/anhydrides and dihydroxy alcohols. In unsaturated polyester resins, one of the reactants, either a difunctional acid and/or a dihydroxyl alcohol is generally unsaturated to allow for crosslinking to occur. Particularly useful molecules for introducing unsaturation sites into a polymer backbone can be, for example, maleic acid, maleic anhydride and fumaric acid. Maleic anhydride is generally preferable in the synthesis of unsaturated polyester due to its low cost.

Ink polymer bases with unsaturated polyesters generally contain an unsaturated acid and/or unsaturated anhydride, for example, maleic acid and/or maleic anhydride. A dihydroxyl alcohol, for example, a glycol, that joins the acids together is generally incorporated into the polyester. Suitable glycols include for example, ethylene glycol, propylene glycol, diethylene glycol, dipropylene glycol, NeoPentyl Glycol (NPG) and the like.

Polymer bases of unsaturated polyester inks may also contain a secondary, i.e., additional, saturated difunctional acid, for example, orthophthalic

acid, isophthalic acid, adipic acid, succinic acid and/or succinic anhydride, other saturated acids and anhydrides thereof. A secondary saturated acid is generally included in the polymer base in order to reduce the crosslinking and rigidity relative to an all unsaturated acid polymer base.

A number of suitable resins that include unsaturated polyester resins with a saturated secondary acid are commercially available and can be purchased from, for example, Cook Composites and Polymers (CCP), Kansas City, MO. The commercially available unsaturated polyester resins are generally referred to by the type of the saturated acid that is included in the resin since generally all of the unsaturated polyester resins include maleic acid and/or maleic anhydride moieties. An isophthalic resin obtained from CCP, for example, includes a polyester formed from maleic anhydride moieties, isopthalic acid moieties and a glycol. Suitable inks include, for example, orthophthalic resins, isophthalic resins, and dicyclopentadiene (DCPD) resins. Vinyl ester resins may also be suitable. Preferably, the inks include a maleic acid/isopthalic polymer base, and more preferably a maleic acid/isopthalic/neopentyl glycol polymer base.

Inks comprising vinyl esters may also be suitable. Vinyl esters can be prepared by reacting a monofunctional unsaturated acid such as methacrylic acid or acrylic acid with a bisphenol diepoxide. The

resulting polymer which contains unsaturated sites only in the terminal positions is mixed with an unsaturated monomer such as styrene.

The inks with the desired polymer base resins may be clear, white, black and/or contain any number of other color pigments. These inks may be used in a desired manner to generate the desired images. Desirable inks contain pigments that are light stable, i.e. do not yellow after prolonged exposure to ultraviolet light. The selection of the color pigments in the ink is based on the desired image to be created on the decorative transfer. A number of colored resins with the polymer base are commercially available. If the desired color of the ink is not commercially available, one or more inks may be combined to achieve other desired colors. Color matching as known in the art may be performed using the commercially available ink colors. Additional pigments can be added to the polymer base resins as desired.

In embodiments where a metallic color is desired, a clear or transparent ink may be used and metallic powders can be blended into the transparent ink to achieve the desired effect. Metallic powders that can be blended into the inks include, for example, aluminum, copper and the like. A pearlescent pigment may also be blended into the transparent ink.

The inks can also include agents that affect the viscosity of the ink. Gelling agents that increase the viscosity of the ink may be included in the

commercial polymer base resins or added to commercial polymer base resins to obtain a desired viscosity. Gelling agents can include, for example, a fumed silica, such as Cab-O-Sil.

Solvents are generally included in the inks. Solvents can aid in the suspension and/or solubilization of the ink components. Additional solvents that "thin" the inks, referred to herein as thinning solvents, may be added to commercial polymer base resins to obtain an ink with a desired viscosity, dry time and/or flow characteristics. Increasing the amount of solvents in the inks generally decreases the viscosity of the ink and thus, affects the flowability of the ink.

Suitable thinning solvents can also be selected based on their evaporative characteristics. In screenprinting, for example, thinning solvents that evaporate relatively slowly, are added to the ink in order to reduce drying in the screen. Suitable thinning solvents that can be included in the inks include, for example, ketones such as cyclohexanone, isopherone, butrolactone and combinations thereof. The thinning solvent is preferably 9630 polyester thinner purchased from Nazdar Company, Inc., Shawnee, KS that includes petroleum distillate, cyclohexanone, butrolactone and napthalene. Addition of a thinning solvent may not be necessary if drying of the ink during image creation is not an issue. The desirable amount and type of thinning solvent can vary and may depend on the technique used

for creating the image on a backing and the desired time of drying the image on the backing. Preferably, about 3 percent by weight to about 15 percent by weight of the thinning solvent is added to the inks and more preferably from about 5 percent by weight to about 10 percent by weight of the thinning solvent is added to the inks.

The solvents included in the ink generally evaporate, in a reasonable period of time, to produce a dry image after the ink has been applied to the backing. The solvents generally evaporate to produce a dry image by about ten minutes to about 2 hours when air dried at room temperature, preferably between about 15 minutes and about 60 minutes, and more preferably between about 20 minutes and about 40 minutes. The drying time may be decreased by drying, for example, in an oven at an elevated temperature. The decorative transfer with the image may be dried, for example, at about 150°F-200°F. In order to facilitate faster drying times, additional protocols generally known in the art can be used to dry the images and include exposing the image to heat, to a fan and the like.

The inks may include silicone flow agents that affect the flowability of the ink. Suitable silicone flow agents include, for example, ML-520 flow promoter purchased from Cudner & O'Connor Co. Chicago, IL. The inks may also include ultraviolet light absorbers that can better protect the image against degradation caused by exposure to sunlight. Suitable

ultraviolet light absorbers include, for example, Cyasorb UV-531, UV-24, UV-9 benzophenone absorbers and Cyasorb UV-5411 benzotriazole absorber that can be purchased from American Cyanamid Co. Newark, N.J.

In order to create the image, a number of techniques may be used. These techniques include screenprinting the image, spray painting the image, air-brushing the image and the like. Printing techniques can be conventional and include, for example, screenprinting the images onto the inner surface of the backing. Printing on water slide release carrier is disclosed in U.S. patent 4,337,289 to Reed entitled "Water Release Transfer," which is incorporated herein by reference.

In preferred embodiments, the images are screenprinted using the crosslinkable inks described above. The viscosity of the inks can be adjusted to obtain the desired flow properties for use in screenprinting. In the example described herein, the inks formed from pigmented polymer base resins were obtained from CCP, Kansas City, MO. and additional thinning solvent and silicone were added to obtain an ink with the desired flow properties and drying time for screenprinting. Advantages of screenprinting images include higher efficiency, complex image production, sharper images and the like. The image layers can have a selected thickness. In screenprinting, the thickness of the image can be controlled by the screen mesh size and also by ink

characteristics. The thickness of the image layer is preferably between about 5 microns to about 25 microns and more preferably the thickness of the image layer is between about 10 microns and about 20 microns.

The image layers may form a continuous film so the individual portions of the image will remain together. If a background layer is printed in place, the thin background film of ink will be transferred along with design or words that are overprinted. The transferable image on the backing may include one or more clear, or solid colored compatible ink layers. In the case where a plurality of ink layers are superimposed to form a composite design, the inks are applied sequentially and each layer is subjected to a degree of drying to the extent necessary to accept overprinting without picking or smudging before application of the succeeding layers. It is preferable to fully dry the intermediate layers before applying the subsequent layers.

Multilayer images usually consist of one or more colored design layers printed as a film. Both single-layer and multi-layer printing on the backing result in the overall film or layer of printing that remains intact so it can be placed on the sticky surface of the clear outer gel coat without damage. The present method makes transfer easier than other methods, since the sticky or tacky surface of the clear outer gel coat holds the image together. In embodiments with the water slide carrier layer, the

easy release of the backing from the image design layer also is an important feature when transferring films of thin images and coatings, such as those preferably used with the present technique.

When the image is dry, the decorative transfers are ready for use. The decorative transfers can be stacked and/or stored for future use. When stacked, each individual decorative transfer may have slipsheeting to prevent sticking. The decorative transfer, once dry, may be sold, with or without wrapping. The decorative transfer preferably is stored away from heat, direct sunlight, high humidity or other conditions that may deteriorate the quality of the image and/or the decorative transfer. Alternatively, the decorative transfer can be immediately applied to the tacky surface of the clear outer gel coat.

B. Molded products

The methods described herein can be used to produce a variety of molded products. The molded products include an image protected by a clear outer gel coat, a color gel coat and generally an additional molded structure. The image in the molded product, preferably, includes an ink that has a crosslinked polymer base.

Molded products as described herein include products that contain decorative transfers, for example, boats, snowmobiles, water skis, jet skis, recreational vehicles, gel coat parts of automobiles, bathtubs, showers, tabletops, furniture and the like.

Molded products, as referred to herein, also include parts of molded products, i.e. front end, back end, engine cover, top etc., that will ultimately be used in combination with other parts to make the desired product.

The molded products described herein can be made using an open mold process or a closed mold process. Molded products and/or parts made using an open mold process have one surface, i.e. the exterior surface, that was in contact with a mold surface during the molding process. Molded products and/or parts using the closed mold process, however, generally have two surfaces, i.e. the interior surface and the exterior surface, that were in contact with a mold surface during the molding process.

In preferred molded products, the clear outer gel coat, the polymer base of the ink in the image, the color gel coat and the support resin of the molded structure generally have been co-crosslinked by exposure to a catalyst for a suitable time. The image in the molded product, preferably, is not distorted, puckered or otherwise misaligned. The molded products described herein have particularly durable images due to the protection afforded by the clear outer gel coat layer. The image has exceptional exterior durability, abrasion resistance, impact resistance and water immersion resistance.

C. Application of decorative transfer

The decorative transfers described above are preferably used for placement of images within a molded product. A clear outer gel coat can be applied to a mold surface, preferably to a defined area for placement of the image. The image is adhered to the clear outer gel coat during the tacky state. The backing sheet is removed from the image. A color gel coat and a molded structure can be formed over the image layer prior to crosslinking. Co-crosslinking of the polymers applied to the mold surface results in a molded product with the image embedded between crosslinked polymers and protected by a clear, durable crosslinked material.

To form a molded product with a decorative transfer, a clear outer gel coat is generally applied to a mold surface. The clear outer gel coat can be a catalyzed, but uncured, clear outer gel coat, i.e. the clear outer gel coat can include a catalyst. Alternatively, a catalyst is not included in the clear outer gel coat prior to application to the mold surface.

In preferred embodiments, the clear outer gel coat is applied to the section of the mold surface that is to receive the image. A frame with an opening, i.e. a mask, that has dimensions that are about the same as the dimensions of the image to be applied may be placed on the mold surface prior to applying the clear outer gel coat. The clear outer gel coat is then applied to the section defined by the opening of the

frame. The use of the frame results in clear outer gel coat being applied to only the region of the mold surface that is to receive the image. The frame may be removed once the clear outer gel coat acquires the appropriate tackiness. In alternative embodiments, the clear outer gel coat may be applied to the entire mold surface or other portions thereof substantially larger than the image.

The clear outer gel coat to be applied to a mold surface can be selected from a variety of commercially available gel coats that provide water and fade resistance when in use, as well as blister resistance. The clear gel coat is generally applied to the mold surface by spray equipment.

The clear outer gel coat can include polymers such as polyester resins, preferably unsaturated polyester resins. Polyester resins can include ortho resins, iso resins, bisphenol A fumarates, chlorendics and vinyl esters. Polyester resins generally are formed by the reaction between polyfunctional acids and polyhydroxyl alcohols and preferably between difunctional carboxylic acids/anhydrides and dihydroxyl alcohols. In unsaturated polyesters, one of the reactants, either a difunctional acid and/or a dihydroxyl alcohol is generally unsaturated to allow for crosslinking to occur. Particularly useful molecules for introducing unsaturation sites into a polymer backbone can be, for example, maleic acid, maleic anhydride and fumaric

acid. Maleic anhydride is generally preferable in the synthesis of unsaturated polyester due to its low cost.

Unsaturated polyester resins generally contain an unsaturated acid and/or unsaturated anhydride, for example, maleic acid and/or maleic anhydride. Polymer bases for the clear outer gel coat that include only maleic acid and/or maleic anhydride may be used. A dihydroxyl alcohol, for example, a glycol, that joins the acids together is generally incorporated into the polyester. Suitable glycols include for example, ethylene glycol, propylene glycol, diethylene glycol, dipropylene glycol, NeoPentyl Glycol (NPG) and the like.

Unsaturated polyester resins may also contain a secondary, i.e. additional, saturated difunctional acid, for example, orthophthalic acid, isophthalic acid, adipic acid, succinic acid and/or succinic anhydride, other saturated acids and anhydrides thereof. A secondary saturated acid is generally used in the polymer base of the clear outer gel coat in order to reduce the crosslinking and rigidity relative to an all unsaturated acid polymer base.

A number of suitable polyester resins for the clear outer gel coat are commercially available and can be purchased from, for example, Cook Composites and Polymers, Kansas City, MO. These resins include, for example, orthophthalic resins, isophthalic resins, and dicyclopentadiene (DCPD) resins. Vinyl esters as

resins may also be suitable. The clear outer gel coat resin preferably is a maleic acid/isopthalic gel coat resin, and more preferably is a maleic acid/isopthalic/NPG® (ISO/NPG®) gel coat polyester resin formulation that can be purchased from Cook Composites and Polymers, Kansas City, MO.

Clear outer gel coat that include vinyl ester polymers may also be suitable. Vinyl esters can be prepared by reacting a monofunctional unsaturated acid such as methacrylic acid or acrylic acid with a bisphenol diepoxide. The resulting polymer which contains unsaturated sites only in the terminal positions is mixed with an unsaturated monomer such as styrene.

The mold surface may be prepared for the application of the clear outer gel coat in a suitable fashion including the application of a mold release agent such as a wax. Suitable mold release agents include, for example, Hi-Low 1000 release wax in paste or liquid, Supreme mold release and Honey wax mold release obtained from Composite One, Arlington Heights, IL. The clear outer gel coat may be applied to the mold surface using a variety of techniques including spraying the clear outer gel coat, applying with an implement such as a brush, a doctor blade and the like. The clear outer gel coat can be applied to the desired region of the desired mold surface. The clear outer gel coat can be applied and built up to obtain the desired depth. The desired depth of the clear outer

gel coat can vary based on the molded product and its use. The clear outer gel coat preferably is applied to a depth of between about .008 inches and about 0.015 inches, more preferably between about .010 inches and about 0.012 inches.

A catalyst can be added to the clear outer gel coat prior to application onto the mold surface. A catalyst, however, is not necessary in the clear outer gel coat if additional polymers that include a catalyst will be applied later over the clear outer gel coat.

The clear outer gel coat can acquire a tacky, adhesive-like characteristic when applied to the mold surface. The clear outer gel coat can maintain the tacky state until exposed to a catalyst at which time crosslinking can occur. Without being bound to any particular theory, it is believed that the clear outer gel coat acquires the tacky state due to solvent evaporation. In embodiments where a catalyst is incorporated into the clear outer gel coat, the tacky gel state of the clear outer gel coat is in transition prior to crosslinking.

The tacky, gel state is particularly advantageous for applying the decorative transfer. The catalyzed clear outer gel coat generally becomes tacky after about 20 minutes and remains tacky for between about 30 minutes and about 120 minutes. Clear outer gel coat without added catalyst, however, may not become tacky until at least about 100 minutes and will remain tacky until exposure to catalyst. The duration

of the tacky gel state of the clear outer gel coat may depend on a number of factors including, for example, ambient temperature. Application of heat, for example, on the catalyzed clear gel coat may decrease the time required for the polymers to become crosslinked, thus the duration of the tacky state may be decreased.

Suitable catalysts for crosslinking the clear polyester outer gel coat are commercially available. Catalysts can be purchased, for example, from Advanced Plastics, Nashville, TN. Suitable catalysts include organic peroxides, for example, methyl ethyl ketone peroxide and benzoyl peroxide. In preferred embodiments, the catalyst is methyl ethyl ketone peroxide. The catalysts can be added to the clear outer gel coat at a concentration of between about 1.5 percent by weight and about 3.0 percent by weight of the gel coat and preferably at about 2.0 percent weight of the gel coat.

The amount of catalyst may be adjusted depending on the ambient temperature and/or humidity. As the temperature and/or humidity increases the amount of catalyst added may be lower. Conversely, as the temperature and/or humidity decreases the amount of catalyst added may be higher.

When the clear outer gel coat achieves the tacky state, the decorative transfer can be applied with the image layer against the tacky surface. The image layer is preferably applied when slight thumb pressure against the tacky clear outer gel coat does

not leave a fingerprint, and the clear outer gel coat does not stick to the finger. In the tacky state, the clear outer gel coat has essentially pressure-sensitive adhesive characteristics and will cause the image layer to adhere to the clear outer gel coat and also not slip when additional materials are applied against the image layer. The tacky surface generally grips the image layer.

Once the image layer is in contact with the tacky surface of the clear outer gel coat, the backing of the decorative transfer can be removed. The backing generally is removed prior to complete crosslinking. Preferably, the backing is removed shortly after the image has adhered to the tacky clear outer gel coat. Methods for removing the backing from the decorative transfer can vary depending on the type of backing used. The backing is preferably removed with little or no perceivable distortion of the image. In embodiments with a water slide release liner backing, the backing can be removed by applying water to penetrate the paper backing and release the image layer onto the tacky surface.

Additional crosslinkable polymers are preferably applied over the image after removal of the backing. In preferred embodiments, a color gel coat is applied over the image layer. The color gel coat generally determines the color of the molded product and the background color of the image. The color of the color gel coat is thus, selected based on the

desired background color of the molded product. The use of the color gel coat results in an image that is ultimately embedded within crosslinked polymers.

In some embodiments, only one color gel coat may be applied over the entire mold surface including the section of the mold surface with the adhered image. In other embodiments, a plurality of color gel coats may be used. If using a plurality of color gel coats, the color gel coats may be applied adjacent to each other and/or in layers over each other. Different color gel coats, for example, may be applied to different areas of the molded surface to obtain a molded product with a variety of background colors. If two or more color gel coats are applied, each of the color gel coats is generally applied sequentially but prior to complete crosslinking of any of the polymers.

The color gel coat layers are generally compatible with the clear outer gel coat and the image layers. The color gel coat can include any of the polymer bases, solvents and other compounds described above for the clear outer gel coat. The color gel coats preferably also includes one or more pigments, metallic powders and the like. Thus, color gel coats as described herein can be any of the clear outer gel coats described above with the addition of compounds that produce the desired color, including, for example, white. While a colored pigment is generally desired in the color gel coat, the color gel coat can be clear, if desired.

A catalyst is generally added to the color gel coat prior to application over the image and/or the mold surface. Preferably, the catalyst in the color gel coat is the same as the catalyst in the clear outer gel coat, if present. The clear outer gel coat and the color gel coat, however, may have a different catalyst. The color gel coats may be applied by any method described above for the clear outer gel coat. The color gel coats are generally sprayed onto the mold surface.

The color gel coats can generally have any desired thickness. In some embodiments, the color gel coats have a thickness of between about 0.015 inches and about 0.125 inches, preferably between about 0.030 inches and about 0.065 inches.

In principle, the color gel coat could be applied at a sufficient thickness to produce the final molded product. However, a molded structure is generally formed on the mold surface over the color gel coat prior to complete crosslinking of the polymers already present on mold surface. The molded structure can include one or more reinforcing substrates and a crosslinkable support resin. The molded structure is generally formed by layering reinforcing substrates and the crosslinkable support resin, preferably in an alternating fashion. A reinforcing substrate, for example, may be placed over the color gel coat, then the support resin, followed by another substrate, then

additional support resin and so on until the desired structure is formed.

Reinforcing substrates for forming the molded structure described herein can include a variety of materials. Suitable reinforcing substrates include, for example, fiberglass, carbon fiber, kevlar, foam, balsa wood, angelhair and the like. The substrates are generally in the form of a mat, a weave and the like such that the support resin penetrates through the substrate. To form the molded structure, only one type of substrate may be used throughout the molded structure. Alternatively, a combination of substrates may be used in forming the molded structure.

The crosslinkable support resin is generally used as a "wetting compound" to hold the substrates down onto the mold surface and also to ultimately provide a network of crosslinked polymers within and around the substrates. Upon crosslinking, the combination of the support resin and the substrates form a durable, resilient structure that is suitable for the functioning of the molded products described herein.

The crosslinkable support resin can include a variety of suitable crosslinkable polymers. Preferable crosslinkable support resins can include any of the polymers or combination of polymers described above for the clear outer gel coat and the color gel coat. The support resin may be clear. Alternatively,

the support resin may be tinted by the addition of a tint additive.

A catalyst is generally added to the support resin prior to use. Preferably, the catalyst in the support resin is the same as the catalyst in the clear outer gel coat and/or the color gel coat. The support resin, however, may have a catalyst that is different from the clear outer gel coat and the color gel coat.

The specific type of substrates, the number of substrate layers, and the application of the support resin is referred to as a lamination schedule. The lamination schedule is generally determined by the end use of the molded product. In example 2 below, multiple layers of glass mat were used as the substrate along with a catalyzed polyester resin until the desired thickness was generated.

The substrates and the support resin are generally applied prior to complete crosslinking of the other polymers on the mold surface. After application of all the substrates and the support resin, the outermost, exposed surface is preferably smoothed. The exposed surface may be smoothed, for example, using brushes, squeegees, steel rollers, plastic rollers and the like. In embodiments using a close mold process, a second mold surface may be contacted with the outermost surface of the molded structure prior to complete crosslinking. Crosslinking will start once polymer and catalyst are mixed. But the process is set up to take some time to complete. It is complete crosslinking

that is avoided since adjacent layers then will not bind.

In the molded product, the clear outer gel coat, polymer base in the ink, the color gel coat and the support resin are preferably compatible, and more preferably include equivalent crosslinkable polymers. The polymer bases for each of these layers can be selected such that co-crosslinking of the polymers results in a monolithic structure. The use of incompatible polymers may result in an image that is puckered, distorted and/or a molded product that is less durable.

The mold surface with the polymers is generally allowed to cure. The length of curing may depend on the types of various polymer bases present in the different layers and the catalyst used. Preferably, the structure on the mold is allowed to cure for at least several hours, more preferably at least overnight and even more preferably for at least about 24 hours.

The clear outer gel coat, the image layer, the color gel coat, and the molded structure are generally left on the mold surface in order for the crosslinking to occur. During this period, the polymers in each of the layers generally become crosslinked. The co-crosslinking of the polymers in all the layers thus, forms a monolithic-type structure with an image that is particularly durable due to

protection afforded by the crosslinked clear outer gel coat.

The crosslinked product can be removed from the mold surface using conventional techniques in the art. Generally the molded product comes off the mold surface, due to the presence of the mold release agent, when a small section is pried away. The molded product has an image that is preferably crosslinked, visible through and protected by a crosslinked clear outer gel coat.

In some embodiments, if the ink used to create the image was non-crosslinkable, only the clear outer gel coat, the color gel coat and the support resin of the molded product are crosslinked. The image, however, is still visible through and protected by a crosslinked clear outer gel coat.

The molded product with the image, once removed from the mold surface, may be used in a suitable manner depending on the nature of the product. If the molded product is a boat, for example, the product may be processed in a conventional manner such as incorporating an engine, windshield, seating and the like.

In this way, the use of the process for providing a decorative transfer that is protected by an outer clear coat is achieved at a minimum of expense, and without die cutting or the like. Decorative transfers are relatively easy to print and an image in an ink or material that is crosslinkable, compatible

with the clear outer gel coat being used is particularly advantageous.

EXAMPLE

Example 1-Decorative transfer with crosslinkable ink

This example illustrates a method for making a decorative transfer using crosslinkable ink.

The CCP 953 WJ 300 series of polyester gel coats were purchased from Cook Composites and Polymers, Kansas City, MO. To these gel coats, about 5 to about 10 percent by weight of 9630 polyester thinner from Nazdar Company, Inc., Shawnee, KS and about 2 percent or less by weight of ML-520 flow promoter from Cudner & Connor Co., Chicago, IL. were added to form a screenable ink. The polyester gel coat, the solvent and the flow agent were mixed together prior to use in screen printing. Mixing was performed with a conventional paint shaker. Additional solvent and flow agent were added, if necessary, to obtain the desired screenability of the inks.

Special opaque colors and shades were produced by blending appropriate quantities of CCP 953 WJ 300 series colors together. For example, a gray color was produced with a blend of about 2.0 percent by weight of 953 WJ 300 series black and about 98.0 percent by weight of 953 WJ 301 series white. Different shades of gray can be obtained by varying the weight percent of the black and the white gel coats.

Transparent and metallic colors were produced by blending appropriate quantities of CCP 942

XA 220 clear polyester gel coat with liquid pigment concentrates purchased from American Colors, Elberta, AL and metal pigments purchased from Alcoa, Bauxite, AR. A transparent metallic red was made by using about 90 percent by weight of 942 XA 220 clear polyester gel coat, about 8 percent by weight of red concentrate liquid pigment, and about 2 percent by weight of aluminum powder.

The screening equipment included conventional off contact screening equipment, vacuum tables, screen fabrics, stencils, and squeeges. The inks were placed onto the screen and squeeged to form the image. The inks with additional solvents and flow agents had improved ink flow characteristics and reduced tendency for drying in the screen. The decorative transfers were air dried at room temperature or oven dried in a convection oven at temperature ranging from about 150°F to about 250°F to remove solvents from the inks.

In order to make a 3 color decoration, the first color was applied on the water slide carrier sheet using conventional edge registration techniques to register the first color in a specific area on the carrier. After the first color dried, the next color was applied with a second screen using edge registration to position the second color in its proper location on the water slide carrier sheet. After the second color dried, the next color was applied with a third screen design using registration to position the

third color in its proper location on the sheet. After all the colors have been applied and dried to remove any residual solvents and leave the screened inks tack free, the water slide carrier sheets can be stacked until ready to use.

Example 2-Application of decorative transfer in a boat

This example illustrates the application of a decorative transfer in a boat mold.

A decorative transfer was made as described in Example 1. The mold was coated with the wax release agent Finish Kare Hi Low relase wax, Composites One, Lino Lakes, MN and allowed to air dry for several minutes. The wax coating was polished to a high gloss with a soft clean cloth.

A die cut paper or plastic paint mask with appropriate openings was applied to the mold surface and held in place with pressure sensitive adhesive. The opening in the paint mask corresponds to the outside dimensions of the decorations screened on to the water slide release carrier sheet that was to be incorporated.

A clear polyester gel coat (CCP 942-XA-220) from CCP, Kansas City, MO. was mixed with about 1.5 percent by weight of the catalyst Lupersol DHD-9 MEKP purchased from Composite One, Lino Lakes, MN. The catalyzed gel coat was precision coated onto the mold surface containing a paint mask to a wet coat thickness of about 0.010 inches to about 0.015 inches.

The coating was air dried for about 15 minutes and the paint mask was removed. The clear gel coat was allowed to dry for another 15 to 30 minutes until the gel coat developed a tacky adhesive-like characteristic when tested with finger pressure.

The decorative water slide transfer was positioned over the tacky polyester clear gel coat and laminated on to the tacky surface with a squeegee to minimize trapped air at the gel coat/decorative transfer interface.

When the water slide transfer was applied and firmly attached to the clear gel coat, water was applied until the backing paper was completely wet. The water was allowed to penetrate into the paper to dissolve the water soluble coating. The carrier was removed leaving only the screened image attached to the clear outer gel coat.

A pigmented white polyester gel coat color (953-WJ-301 white) purchased from Cook Composite and Polymers, Kansas City, MO. was mixed with about 1.5 percent by weight of the catalyst Lupersol DHD-9 methyl ethyl ketone peroxide. The catalyzed white gel coat was sprayed over the image and also the mold surface area surrounding the image to a wet coat thickness of about 0.125 inches. The whole composition was allowed to set for about 25 minutes to about 30 minutes prior to addition of the lamination schedule.

A molded structure of polyester resin/glass mat lamination was applied to complete the component

construction. A solution of Reichold polylite polyester resin from Cook Composites and Polymers, Kansas City, MO, catalyzed with DHD-9 MEKP (red dye) MEK 46736 from Advanced Plastics, Nashville, TN, was applied to the white gel coat followed by lamination of glass mat. The red dye in the catalyst was added to provide a visual aid to determine thickness and coverage of the applied coatings. The lamination schedule included one layer of angel hair fiberglass, one layer of 20 ounce core Mat, and 3 layers of continuous strand fiberglass mat purchased from Owens-Corning Fiberglas. A coating of resin was applied prior to application of each layer of the fiberglass/core mats. This lamination schedule resulted in a molded structure of between about 3/4 inch and about one inch. The end use of the molded product determined the desired thickness and strength and thus, the lamination schedule. The whole composition on the mold surface was allowed to cure for between about 12 to about 24 hours at room temperature.

The fabrication of the molded component was complete at this point. The finished part was removed from the mold surface using conventional techniques. When the molded component was removed and viewed in plan view, the image was embedded behind a layer of clear polyester gel coat surrounded by a colored (white) gel coat. The image was smooth to the touch, did not protrude from the surface and was at the same

height as the surrounding surface. The molded component was used to continue the assembly process.

Although the present invention has been described with reference to preferred embodiments, workers skilled in the art will recognize that changes may be made in form and detail without departing from the spirit and scope of the invention.

WHAT IS CLAIMED IS:

1. A decorative transfer comprising a backing sheet and an image layer on the inner surface of the backing sheet, the image layer comprising a film of an ink, wherein the ink comprises a crosslinkable polymer base.

2. The decorative transfer of claim 1 wherein the ink comprises an unsaturated polyester resin.

3. The decorative transfer of claim 1 wherein the ink comprises an unsaturated polyester resin with saturated and unsaturated polycarboxylic acid moieties incorporated into the resin polymer.

4. The decorative transfer of claim 1 wherein the image layer comprises screened ink.

5. The decorative transfer of claim 1 wherein the ink is crosslinked when exposed to a catalyst.

6. The decorative transfer of claim 1 wherein the crosslinkable polymer base comprises maleic acid moieties polymerized with dihydroxy alcohols.

7. The decorative transfer of claim 1 wherein the ink comprises isopthallic/neopentyl glycol® resin.

8. A molded product comprising an image layer and a clear outer gel coat covering the image layer, the clear outer gel coat comprising a polymer base that is crosslinked.

9. The molded product of claim 8 wherein the image layer comprises a film of an ink comprising a crosslinked polymer.

10. The molded product of claim 9 wherein the polymer base of the ink in the image layer is compatible with the polymer base of the clear outer gel coat layer.

11. The molded product of claim 9 wherein the polymer base of the ink in the image layer comprises an equivalent polymer as polymer base of the clear outer gel coat.

12. The molded product of claim 9 wherein the polymer base of the clear outer gel coat and the ink both comprise an isopthallic/neopentyl glycol® resin.

13. The molded product of claim 9 further comprising a color gel coat.

14. The molded product of claim 8 further comprising a molded structure comprising one or more layers of substrate and crosslinkable support resin, the substrate and the support resin combined to form the molded structure of the molded product upon crosslinking.

15. The molded product of claim 8 wherein the molded products are selected from the group consisting of boats, shower stalls, snow mobiles, jet skis, water skis, recreational vehicles, automobile components, aircraft components and parts thereof.

16. A process of providing a decorative transfer comprising the step of creating an image onto a backing sheet, wherein the image is screen applied to the backing sheet with an ink that crosslinks upon exposure to a catalyst.

17. The process of claim 16 wherein the ink comprises an unsaturated polyester resin.

18. The process of claim 16 wherein the ink crosslinks upon exposure to a catalyst comprising methyl ethyl ketone peroxide.

19. A process for making a molded product with a decorative transfer comprising:

applying a clear outer gel coat onto a mold surface wherein the clear outer gel coat attains a tacky surface; and

placing a decorative transfer comprising an image layer and a backing sheet onto the tacky surface of the clear outer gel coat with the image layer in contact with the tacky surface.

20. The process of claim 19 wherein the image layer comprises a film of crosslinkable ink on the inner surface of the backing sheet.

21. The process of claim 20 wherein the ink comprises unsaturated polyester resin.

22. The process of claim 19 wherein the image is screen applied to the backing sheet.

23. The process of claim 19 wherein the clear outer gel coat is applied to an area of the mold surface that is to receive the image, the area having dimensions about similar to the outside dimensions of the image.

24. The process of claim 19 wherein the clear outer gel coat comprises a catalyst.

25. The process of claim 19 wherein a plurality of decorative transfers are applied.

26. The process of claim 19 further comprising the step of releasing the backing sheet from the decorative transfer.

27. The process of claim 26 further comprising the step of adhering the image to the tacky surface to maintain the image from slipping when the backing sheet is released.

28. The process of claim 26, further comprising applying a release agent to the backing sheet to remove the backing sheet while the image adheres to the tacky surface.

29. The process of claim 20 wherein the clear outer gel coat and the ink both comprise unsaturated polyester resin.

30. The process of claim 26 further comprising applying a color gel coat to the mold surface, the mold surface comprising the clear outer gel coat with the adhered image layer, the image layer comprising a film of crosslinkable ink.

31. The process of claim 30 wherein the color gel coat comprises a catalyst.

32. The process of claim 31 wherein the catalyst in the color gel coat catalyzes the crosslinking of the color gel coat, the clear outer gel coat and the ink.

33. The process of claim 30 further comprising forming a molded structure over the color gel coat, the

structure comprising one or more substrates and one or more layers of crosslinkable support resin.

34. The process of claim 33 wherein the one or more substrates and the one or more layers of support resin are layered to form a molded structure upon crosslinking.

35. The process of claim 34 wherein the resin comprises a catalyst.

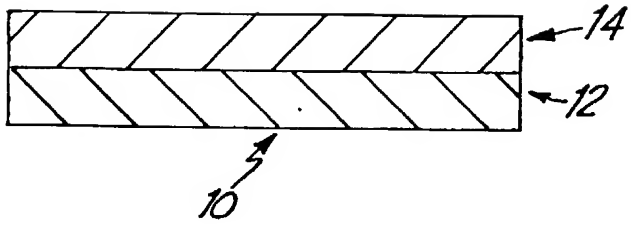

FIG. 1

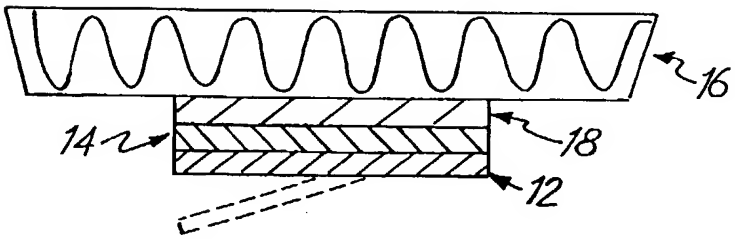

FIG. 2

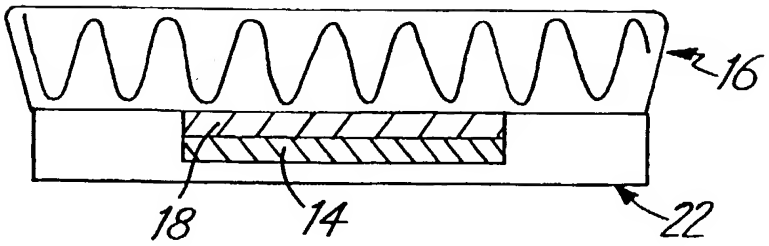

FIG. 3

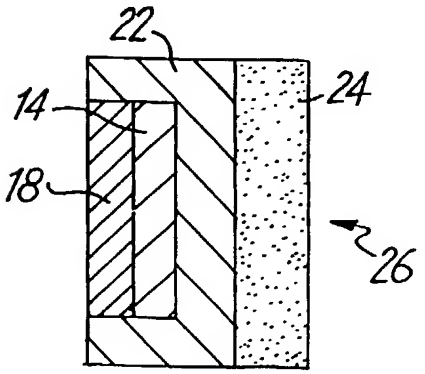

FIG. 4

INTERNATIONAL SEARCH REPORT

Interna al Application No
PCT/US 00/19799

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 B29C37/00 B44C1/17

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 B44C B29C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
WPI Data, PAJ, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 2 236 982 A (DARBY NORMAN PERRY DAVID) 24 April 1991 (1991-04-24)	1-6, 8-11,13, 14,16-18
Y	page 6, line 1 - line 29	7,12, 20-22, 25,29-35
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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"O" document referring to an oral disclosure, use, exhibition or other means

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
18 October 2000	30/10/2000

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Van Nieuwenhuize, O

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INTERNATIONAL SEARCH REPORT

Internat al Application No
PCT/US 00/19799

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